REPORT OF THE CHIEF OF THE BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, 1945

UNITED STATES DEPARTMENT OF AGRICULTURE,
Washington, D. C., September 28, 1945.

MR. P. V. CARDON,
Agricultural Research Administrator.

DEAR MR. CARDON: I present herewith the report of the Bureau of Agricultural and Industrial Chemistry for the fiscal year ended June 30, 1945.

Sincerely,

ORVILLE E. MAY, *Chief.*

INTRODUCTION

THE broad objective of the Bureau of Agricultural and Industrial Chemistry is to gain new scientific and technical knowlwedge required for the conservation of agricultural materials and for the efficient conversion of such materials into manufactured products for food, feed, and other uses.

The Bureau comprises four large regional research laboratories, each having from six to eight research divisions, and nine other divisions and laboratories, two of which were organized for temporary collaborative research supported by allotments from special appropriations.

The purpose of the research in the regional laboratories is to develop outlets for farm commodities (and their products and byproducts), especially for those commodities of which there are frequent surpluses. The commodities that have received attention since the completion of the regional research laboratories during the fiscal year 1941 are: Corn, wheat and other grains, soybeans, and crop residues in the northern region; cotton, cottonseed, sweetpotatoes, and peanuts in the southern region; tobacco, apples, potatoes, vegetable wastes, tanning materials, milk products, animal fats, hides, and leather in the eastern region; and alfalfa, fruits, potatoes and other vegetables, wheat proteins, and poultry products and byproducts in the western region.

Although there is wide diversity in farm commodities, the principal components of these commodities are comparatively few in number, and often different commodities do not differ as to their principal components, but only in the relative proportions of these components. Some of the work of the regional laboratories is organized on a commodity basis, but much of it is organized on the basis of components

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that are common to several or many commodities or on the basis of the type of scientific knowledge applied in the research activities.

In the other divisions and laboratories of the Bureau, research is directed toward the problems of processing and utilization of products of pine gum, tung nuts, sugar plants, citrus and other fruits, and preservation of cucumbers and other vegetables by brining. Special technological research has been conducted on the pilot–plant extraction of rubber from young guayule plants and is about to begin on the production of motor–fuel alcohol and useful byproducts from crop wastes. Fundamental chemical and biological research is in progress on the allergenic components of certain substances from agricultural sources, on the nature and control of enzyme action, on the toxic effects of substances that may contaminate or exist in foods and feeds, on substances that exhibit special biological activity in or toward plants, and on the survival of pathogenic micro–organisms in processed foods.

The Bureau helps farmers and fruit growers by finding industrial outlets for their products, byproducts, and wastes. It cooperates with organizations of producers that are engaged also in processing the crops. It also helps producers of crops for processing by determining the relative suitability for industrial utilization of different varieties of the same plant, so that a proper selection can be made to get a crop that will be acceptable for a particular industrial use. For example, certain varieties of soybeans have been found to be better than others as a source of oil for use in paint and varnish, and certain varieties of sweetpotatoes have been found to be better than others as a source of starch. Likewise, some varieties of fruits and vegetables have been found to be better than other varieties of the same fruits and vegetables for preservation by freezing or dehydration.

Some of the research of the Bureau is in collaboration with State agricultural experiment stations and educational institutions, and some is in collaboration with other bureaus of the U. S. Department of Agriculture and other Federal agencies. Much of it is in collaboration with industrial firms and associations, under cooperative agreements or memoranda of understanding. At the close of the fiscal year 1945, 13 cooperative agreements and 62 memoranda of understanding were in effect.

Some of the more outstanding accomplishments of the Bureau during the fiscal year 1945 are reported in the following pages. More complete and detailed information concerning the work is given in the 299 publications issued during the year. Information on newly developed processes and products is given in the specifications of the 37 public service patents granted during the year to employees of the Bureau. A list of publications issued and patents granted during the fiscal year 1945 is available in mimeographed form.

RESEARCH NEEDED TO MAINTAIN COTTON CONSUMPTION

The results of a recent survey by the Southern Regional Research Laboratory on the development and use of rayon and other synthetic fibers were published as a mimeographed circular. This survey showed that there has been marked expansion in the production and consumption of artificial fibers, especially during the last few years.

Improvements in quality and reductions in price have been major factors in the great expansion of rayon consumption during the last

20 years. Most of the expansion has been in apparel and household fabrics, where appearance is the most important consideration. However, the development of high-strength rayons led to the use of rayon in cord-fabrics for bus, military vehicle, and airplane tires, with consequent large reduction in the consumption of cotton for tire cord.

The artificial fibers in commercial production have found uses in many, but not all, types of textiles. Some of their properties are distinctly different from those of the natural fibers, making them better suited for particular purposes.

It is believed that the maintenance of cotton consumption depends upon the reduction of cost and improvement in quality of cotton products, and that these depend upon research in all branches of cotton production and processing. The development of new and improved cotton products that will give the consumer greater satisfaction than he can obtain from other materials seems to be essential if cotton is to compete successfully with artificial fibers.

BETTER COTTON TIRE CORDS IN PROSPECT

The report for 1944 mentioned a "dual-stretch" process that had been developed for improving the quality of cotton tire cords. In this process the wetted cord was stretched under a high tension (just short of the breaking point) in hot air until dry to impart the maximum tensile strength, and then the cord was wetted and restretched at room temperature until dry under a definite lower tension that would allow the cord to regain a limited degree of its original stretchability without losing much of the extra strength imparted by the first treatment.

In the fiscal year 1945 four service tests under the supervision of the United States Army and the War Production Board were completed on tires made with cords manufactured from selected varieties of cotton. Two service tests had been carried out previously. These six tests showed beyond a doubt that cords manufactured from Wilds 13, SXP, and Stoneville 2B varieties of cotton made stronger tire carcasses than were made from the regular run of commercially produced cotton tire cord of similar construction. Truck tires containing cord manufactured from the Wilds 13 cotton gave outstanding service in comparison with similar tires containing the regularly used commercial cotton cord. Therefore, particular attention was directed toward the production of superior tire cord from the better varieties of cotton.

From the service tests made last year, much additional information was gained with regard to the influence of cord diameter (gage) and construction on tire performance, and this served to guide further research on the development of improved types of cotton cord. The results of service tests on cotton cords in comparison with rayon cords were not conclusive, but it appeared, on the basis of tests made by the Government Tire Test Fleet and the results of laboratory studies on hysteresis in different parts of tire casings, that in order for cotton cord to compete with rayon cord in synthetic-rubber truck tires, the cord will have to be low-gage, or the construction of the tire will have to be modified.

A method and necessary equipment were devised for testing tire cords for flexing fatigue; and the effects of variations in temperature,

fiber strength, moisture content, and cord construction on flexing fatigue were determined. Apparatus was constructed for measuring the elastic properties of tire cord, which determine the extent of hysteresis and consequent heat development in the carcass, under different conditions of temperature, moisture content, and load. The results obtained with this apparatus were used to establish better criteria of the desirable properties of tire cord in terms of the functions the cord must perform in the tire.

An improved technique was devised for measuring the adhesion of tire cord to rubber. This is a modification of the commonly used "H" adhesion test, the most important change being the removal of the central cord sheath. Laboratory studies on the adhesive properties of tire cord, when vulcanized in GR–S synthetic rubber after various treatments and under different conditions, showed that the adhesion of cotton tire cord could be increased from 25 to 95 percent by treatment with certain phenolic compounds, such as resorcinol, pyrogallol, and some of their derivatives in combination with formaldehyde and rubber latex.

COTTON FABRICS IMPROVED AND PRESERVED BY CHEMICAL TREATMENTS

The report for 1944 described a newly developed weather-resistant flameproofing treatment, comprising the application of an emulsion containing chlorinated paraffin, a synthetic resin, and suspended antimony oxide, which was satisfactory for clothing fabrics in most respects but allowed the charred portion of the treated fabric to glow for several minutes after removal of the testing flame.

During the last year, efforts were made to eliminate glowing (flameless combustion) on the edges of the treated fabric. Incorporation of zinc borate or of specially prepared zinc ammonium phosphate and magnesium ammonium phosphate in the emulsion was not effective. Recently, attention was directed toward the possibility of developing new cellulose derivatives, such as cellulose ammonium phosphates, for incorporation with the flameproofing materials as insoluble glowproofing agents. Research on preparation of such compounds has not been completed.

The United States Coast Guard, with which the Southern Regional Laboratory cooperated in research on flameproofing of fabrics, had samples of cotton drill, such as that used for life-jacket envelopes, treated by the Bureau's emulsion flameproofing process. The Coast Guard stated that the treated fabric offered advantages over that in current use. On its recommendation a commercial use of this flameproofing process was scheduled.

The effectiveness of the acetylation treatment in preserving fabrics against mildew and bacterial rot was confirmed by extensive tests. This treatment partially converts the cellulose of the cotton fiber to cellulose acetate, which cannot be utilized as food by cellulose-destroying micro-organisms. As a practical test, several bags made of acetylated cotton fabric sewn with acetylated cotton thread were filled with sand and left in contact with the soil and exposed to the weather on the grounds of the laboratory at New Orleans, La.

After 2 years these bags were still intact and serviceable. Numerous samples of acetylated cotton fabrics also showed almost complete

resistance to rotting when buried for 6 months in soil especially prepared to have a high content of cellulose-destroying micro-organisms. The most highly acetylated fabrics gave the best results. Since a high degree of acetylation is costly, the fundamentals of the process are being studied with the expectation that greater knowledge of the chemical reaction and its control will permit the production, at materially lower cost, of treated fabrics having moderate acetyl contents but a high degree of resistance to mildew and rot. Some progress has been made toward the development of a continuous process of acetylating cotton piece goods.

Use of acetylated cotton sewing thread in making tents, awnings, and canvas covers would often extend their serviceability. Since acetylation tends to stiffen the thread, experiments are being made on the performance of acetylated threads in commercial-type sewing machines for canvas and on means for improving the flexibility and reducing friction when they are used for sewing.

Preservative treatments for cotton seine twine were studied under a cooperative arrangement with the Fish and Wildlife Service of the Department of the Interior. Two sets of continuous-immersion tests on seine twine in ocean water in Massachusetts and Florida and in river water in Louisiana, as well as the soil-burial test on cotton osnaburg, indicated that a treatment developed by the Southern Regional Laboratory was superior to any of the commercial treatments in current use. This treatment comprises impregnation of the textile with furfuryl alcohol followed by resinification of this unsaturated compound by polymerization within and on the fibers. Additional samples of seine twine were treated with different amounts of furfuryl alcohol by an improved procedure for comparison with other samples, treated with an insoluble compound of copper or zinc or with seine tar, for continuous-immersion tests during the summer of 1945. At the request of a commercial firm interested in the production of durable seine twine, a quantity of twine was treated with resinified furfuryl alcohol for their use in a series of service tests.

A treatment for imparting acid resistance to cotton thread used for sewing up paper bags, for export of triple superphosphate, was developed in cooperation with the Office of Production Research and Development of the War Production Board. It consists of impregnation with a water solution of triethanolamine, followed by careful drying (preferably in an inert atmosphere to prevent spontaneous combustion) or application of the proper quantity of triethanolamine without dilution with water. Two thousand yards of sewing thread were treated with this material for use in a service test. It lost 3 percent in strength while the untreated thread lost 27 percent.

Unlined cotton fire hose was made possible by a combination of treatments that makes a specially constructed and treated cotton yarn, when properly woven into hose, act like linen yarn in rapidly absorbing water and swelling enough to practically close the minute openings in the tightly woven structure, thus permitting the hose to transmit water under a pressure of 60 pounds per square inch without excessive leakage. In this case, the fabric is made relatively watertight by making it more absorbent. Enough water seeps through to keep the fabric wet, and therefore fire-resistant. The desired objective was attained by treating mercerized cotton yarns, which are more absorbent than

ordinary cotton, with a commercial hydroxy ethyl ether of cellulose in alkaline solution and precipitating it on the fiber by neutralization. The supplemental treatment adds to the water absorption of the fibers and their ability to swell on becoming wet. Although this treatment was intended especially to make cotton serve as a substitute for linen in rubberless hose for use in fighting fires in buildings, ships, and forests, it is expected to be useful for the construction of other watertight fabrics. A United States patent (No. 2,352,707), covering the preparation of cotton yarn for water-pressure hose, was granted to the inventor of this process and assigned to the Secretary of Agriculture.

CHEMICAL-COTTON SUPPLY ASSURED BY NEW MACHINE

The report for 1943, in describing cotton-processing research at the Southern Regional Research Laboratory, stated that a disk-type cotton-cutting machine for rapidly reducing lint cotton to short-length fibers resembling linters had been designed, that a small model had been built, tested, and found to be efficient, and that a larger experimental machine of the same kind and accessory equipment were to be built under a special appropriation for the purpose. The facts that only cotton in short lengths, like cotton linters, could be nitrated or acetylated with existing commercial equipment and that the demand for cotton linters for wartime uses threatened to exceed the supply were responsible for this study. Construction and successful operation of the larger machine were expected to remove any danger of an insufficient supply of linter-type cellulose for use in manufacturing guncotton, smokeless powder, acetate rayon, and cellulose lacquers and plastics for war uses.

In the last year the larger experimental cotton-cutting machine and accessory equipment were completed and tested in a commercial linter-purification plant. The feeding and cutting equipment performed satisfactorily, but the compacting device required some modification to operate at the high speed required. Representatives of the War Production Board and of industrial firms who witnessed the final tests believed that the general operating principle of the machine was sound, and that, with some changes, the machine would do the job for which it was intended.

In order to evaluate the proposed changes, which included modification to permit the cutting of both lint cotton and first-cut linters, the War Production Board, believing that the supply of linters for guncotton might become inadequate to meet military demands, arranged for the construction and testing of an experimental cotton cutter embodying the proposed changes. The Southern Regional Laboratory cooperated in an advisory capacity. A linter-purification firm was selected to test the equipment and was delegated to act as general contractor for its construction and installation.

UTILIZATION OF COTTONSEED AND PEANUT OILS AIDED BY NEW KNOWLEDGE OF PHYSICAL PROPERTIES

At the Southern Regional Research Laboratory, extensive studies were made on the physical properties of crude, refined, and modified cottonseed and peanut oils to gain additional knowledge that was needed for developing new modified-oil products and for improving

known products and processes. These studies included calorimetric determinations of the specific heats and heats of fusion of highly hydrogenated cottonseed oil and a number of pure triglycerides, a crystallographic and X-ray investigation of polymorphism of tristearin and highly hydrogenated cottonseed oil, and dilatometric determination of the density and expansibility of a number of pure triglycerides in both the solid and liquid forms. From the calorimetric and dilatometric data, it was possible to estimate, for the first time, the proportions of solid and liquid in a number of plastic fats at different temperatures within the complete melting range.

A systematic study was also made of the variations in density and viscosity of solutions of cottonseed, peanut, and soybean oils in three organic solvents, as influenced by oil concentration and temperature. In each case data were obtained for a complete range of temperatures, beginning with the temperature below which some of the oil would solidify and ending just below the boiling point of the solvent. The data are necessary for designing equipment and devising processes that involve the handling of mixtures of solvent and oil.

The boiling point-vapor pressure-composition relationships in mixtures of cottonseed oil or peanut oil with commercial hexane were determined for various compositions selected to cover a wide range of vapor pressures. The data obtained for cottonseed oil-solvent and for peanut oil-solvent mixtures are practically identical. They are important for determining how the solvent used to extract oil from ground or flaked seed kernels can be removed with the least deteriorative effect or fixation of objectionable color. Preliminary experiments on the heating of cottonseed oil alone and in admixture with hexane indicated that the solvent can be removed safely and completely at temperatures from 160° to 180° F. and that a solvent-extracted oil freed from solvent at such temperatures has a quality equal to that of oil obtained by hydraulic pressing.

Eight articles reporting research results on the physical properties of cottonseed and peanut oils and their hydrogenation products were published in scientific and technical journals during the period covered by this report.

The solvent-crystallization fractionating procedure, previously developed for vegetable oils, was applied to the fractionation of the fatty acids of raw and hydrogenated cottonseed oil, and conditions were determined for the practical separation of liquid and solid acids. The isolation of the liquid fatty acids from cottonseed and peanut oils and their subsequent re-esterification provide a means of producing from these oils certain industrially useful products, such as low-titer oils for sulfonation, which cannot be obtained by fractionation of the oils themselves. Such synthetic oils are being made in sufficient quantity for evaluation by prospective consumers.

SIMPLIFIED PRICING OF PEANUTS JUSTIFIED BY NUMEROUS ANALYSES

In cooperation with the Commodity Credit Corporation, the Southern Regional Research Laboratory made numerous analyses on samples of Spanish, Runner, and Virginia types of peanuts, collected from 11 states and graded by the War Food Administration, to determine if the U. S. Standards for Farmers' Stock Peanuts, originally intended

for peanuts marketed for food uses, could be used also for peanuts marketed for processing into oil and meal.

The standards for farmers' stocks of unshelled Spanish and Runner types of peanuts give consideration to the minimum percentage of sound kernels and the maximum percentages of damaged kernels and kernels of other varieties allowed. Those for the Virginia type of peanuts give consideration to these criteria and also to the size of kernels, because they are usually grown for the edible-nut trade. Large lots of peanuts bought by oil mills for crushing are evaluated on their oil content and probable refining loss as indicated by chemical analysis.

Laboratory determinations in duplicate were made on 379 samples of peanuts conforming to the U. S. standards for grades No. 1, No. 2, and No. 3, and on 44 samples of "unclassified" peanuts. They included: the weight in grams per 100 kernels; moisture, oil, and protein contents in percent on weight of kernels; and the iodine number and free-fatty acid content of the oil extracted from the kernels. The analytical results, which were published in the August 1944 issue of Oil and Soap, indicated in general that all peanuts of a given commercial type and of good to fair quality (U. S. No. 1, No. 2, and No. 3 Farmers' Stock grades), which are grown in the same region, may be expected to yield oil and protein at practically the same rate in proportion to the total percentage of kernels after shelling, and that the oil obtained from various lots of such peanuts may be expected to be of about the same quality from a refining standpoint.

This finding, together with the extensive analytical data supplied, enabled the Commodity Credit Corporation to substantiate a simplified practice in buying peanuts from farmers for crushing into oil and meal. The peanuts are evaluated on the basis of type, region where grown, the yield of sound mature kernels in percent or in pounds per ton, and existing analytical data, instead of on the results of a special analysis of each lot offered for sale. Thus, the buying of oilseed stocks from farmers is not complicated by multitudinous analyses of samples.

DEPARTMENT COOPERATES WITH INDUSTRY FOR SWEETPOTATO UTILIZATION

Last year's report stated that the United States Sugar Corporation had been authorized by the War Production Board to erect a large sweetpotato-starch plant and that such a plant was under construction at Clewiston, Fla. This plant, which was believed to assure the establishment of a permanent sweetpotato starch industry in the United States, was expected to begin operations in the fall of 1944. Wartime difficulties in obtaining delivery of certain items of materials and equipment delayed completion of the plant and the initial test runs, but such runs were scheduled to begin in October 1945, with regular production starting shortly thereafter.

At the beginning of the fiscal year, a cooperative agreement between the Department of Agriculture and the United States Sugar Corporation for mutual assistance in promoting industrial utilization of sweetpotatoes became effective. This agreement provided for cooperative research by this Bureau and by two other bureaus of the Agricultural

Research Administration, the research of this Bureau comprising laboratory investigations and pilot-plant experiments in connection with the manufacture of starch and other products from sweetpotatoes.

During the year, technical advice and assistance were given by technologists of the Southern Regional Research Laboratory, in connection with final details of plant lay-out, accessory equipment units, and tentative procedures for operation and control, to permit translation of the Bureau's process for the manufacture of sweetpotato starch to the large plant. Coordinated investigations in the laboratory, the pilot plant, and the Laurel Starch Factory furnished additional data needed for initial control adjustments of process-water volume, water-solids relationships in screening and handling pulp, pH and limewater balance in the grinding and screening processes, bleaching and modification of the starch, drying, sampling, and testing.

The Southern Regional Laboratory cooperated in the operation of the Laurel Starch Factory, which was limited in 1944 to a period of about 6 weeks because of a short supply (about 55,000 bushels) of starch-grade sweetpotatoes. The operation provided opportunity to demonstrate the effectiveness of improved factory-control procedures and the superior processing quality of the new L–5 sweetpotato, which made up nearly all of the raw material. Starch production was 529,000 pounds, of which about half went to a cotton mill and some laundries, about a fourth to a manufacturer of electric dry cells, and about a fourth to food uses.

Continuous coagulation and concentration of the crude protein in sweetpotato-starch "fruit water" from the centrifugal separation of starch was effected with improved equipment on a semipilot-plant scale, and preliminary experiments indicated the possibility of simple and economical collection of the precipitated proteins on the byproduct pulp by allowing the treated fruit water to percolate through the pulp.

Laboratory findings on the best conditions for growing feed yeast (*Torula utilis*) on the sugar in sweetpotato-starch fruit water were tested successfully on a small-pilot-plant scale. Yields equivalent to 40 percent or more of dry yeast on the weight of sugars in 35-gallon batches of medium were obtained in 50-gallon propagators. A continuous process of growing feed yeast in sweetpotato-starch fruit water, which involves the use of two-stage propagators, was developed on a laboratory scale. In comparison with the batch process, it materially increases the output of yeast per unit of time, reduces the propagator capacity needed for the same output, and requires less aeration. The yeast can be concentrated with high-speed centrifugals, such as used for starch separation. Preliminary experiments indicated the possibility of growing feed yeast in sweetpotato-starch fruit water without first removing the precipitated protein. Simultaneous concentration of the yeast and coagulated crude protein would be the most economical means for recovering these byproducts for use in feeds.

Analytical data on the quantities of crude protein and sugars in waste sweetpotato-starch fruit water during an 84-hour run at the Laurel Starch Factory indicated that recovery of crude protein and propagation of feed yeast, with the same efficiencies as obtained in the pilot-plant trials, and return of the protein and yeast to the

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residual sweetpotato pulp would have produced around 31 tons of byproduct feed containing about 13.5 percent of crude protein, whereas the actual byproduct was 24.5 tons of residual pulp containing 1.69 percent of crude protein.

SWEETPOTATOES DRIED FOR FEED BY SIMPLIFIED METHOD

The successful farm dehydration of sweetpotatoes for feed is largely dependent on the development of a process that can be carried out with low-cost equipment already available on the farm or easily obtainable. A process meeting these requirements, which was developed in cooperative work by the Agricultural Chemical Research Division and the Alabama Polytechnic Institute, consists essentially of finely grinding the sweetpotatoes, pressing them with a cider press to remove part of the water, and drying the pulp while it is being raked by hand on a horizontal heated metal plate. Where sirup-making facilities are available, the expressed juice may be evaporated to a sirup for table use or for mixing with the dried feed. If the sirup is wanted for table use, it is necessary to strain out the coagulated protein before final concentration.

A licker-in roll, which is standard equipment for a cotton-carding machine, was used in making a new type of grinder for sweetpotatoes. Such a roll has spirally arranged teeth which have a tearing action on the sweetpotatoes and yield a pulp from which a large proportion of the water separates under moderate pressure, leaving a meal that can be easily dehydrated in a rotary-type drier. Experiments have been started to determine if the new type of grinder facilitates starch separation from sweetpotatoes, as well as the drying of sweetpotatoes for feed.

NEW EVIDENCE ON VALUE OF LEAF MEALS IN POULTRY FEEDS

The report for last year called attention to the large quantities of vegetable wastes that accumulate at shipping points and processing plants and showed that the leaf meals prepared from some vegetable wastes are as good or better than alfalfa meal in feeds for raising chicks to broiler size.

Further evidence of the value of leaf meals prepared from vegetable wastes as constituents of poultry feeds was obtained in a second group of cooperative feeding tests by the Delaware Agricultural Experiment Station. Slightly higher egg production was obtained with a basic ration to which 1.25 percent of broccoli-leaf meal was added than with a similar ration to which 2.5 percent of alfalfa meal and fish-liver oil were added. The eggs from hens fed on a basic ration to which broccoli-leaf meal and fish-liver oil were added hatched in nearly the same proportion as those from hens fed on a similar ration to which twice as much alfalfa meal and twice as much fish-liver oil were added.

RIBOFLAVIN PRODUCED WITH PREVIOUSLY UNUSED YEAST

Riboflavin is required by human beings, as well as by domestic animals, for growth and the maintenance of health. Methods for its production are of special interest at this time because of the great need for increased supplies of vitamin concentrates for foods and feeds.

Incidental to research at the Northern Regional Research Laboratory on the utilization of fermentation residues as sources of vitamins, or directly as feeds after increasing their vitamin contents by microbiological processes, a method was developed for the production of riboflavin (vitamin B_2) by culturing species of *Candida*, a previously unused genus of the yeast family, on solutions of glucose containing certain supplementary nutrients.

Two species of *Candida* were used in the experiments, and one of them, *Candida flareri*, consistently produced about twice as much riboflavin as the other. The iron concentration of the medium had to be carefully maintained at 0.01 microgram per milliliter in order to obtain good yields of riboflavin. Either more or less iron resulted in poor yields. Since the nutrients required for culturing these microorganisms are usually too rich in iron, special methods were devised for reducing the iron content of the medium. One procedure, which seems adaptable to commercial use, consists of passing the medium through a layer of granular base-exchange material capable of taking up ions of iron and yielding ions of harmless base (sodium or potassium). With media treated in this way, yields of 100 micrograms of riboflavin per milliliter were frequent, whereas the yields by previous fermentation methods were about 20 micrograms per milliliter. Dry products containing 40 milligrams of riboflavin per gram of material (that is, 4 percent of riboflavin) were prepared in the laboratory. Such concentrates may prove to be suitable for increasing the riboflavin content of feeds and even food products.

Several industrial firms have shown interest in the new process, and at least three are carrying on laboratory and pilot-plant experiments to adapt it to commercial use. From the laboratory results of this Bureau, it appears that riboflavin can be produced by this method to sell at about half of the current market price of the chemically synthesized vitamin.

ALLYL STARCH PROMISING FOR USE IN PROTECTIVE COATINGS

Last year's report told about the preparation by the Eastern Regional Research Laboratory of a new starch compound, allyl starch, which dissolves in certain organic solvents to yield a lacquer or spirit varnish that polymerizes after drying and becomes very hard and resistant to the agents that often damage varnished surfaces.

Experiments made during the fiscal year demonstrated that allyl starch (in which two of the three hydroxyl groups in each glucose unit of starch are replaced with allyl groups) can be used successfully as the main ingredient of a spirit varnish for interior furniture and woodwork. In preparing such a varnish, it is desirable to modify the allyl starch with a plasticizing resin so as to minimize the shrinkage which, otherwise, might make the coating crack. In general, when properly formulated, allyl starch varnishes exhibit such properties as would place them in the class of superior finishes. They dry and harden to a mar-resistant coating much more rapidly than the widely used oil- and resin-containing furniture varnishes. The resistance of the hardened finish to hot and cold water and to alcohol and other organic solvents is notably superior to that of currently used commercial furniture finishes.

The method first developed for preparing allyl starch, by treating starch directly with commercial allyl chloride, required a large excess

of the reagent, but another method was devised whereby it is possible to convert three to four times as much starch to allyl starch with the same quantity of allylating agent as used in the first method.

Methallyl starch, which has properties similar to those of allyl starch, was prepared with commercially available methallyl chloride. Also, a number of completely substituted mixed ethers of starch, containing alkyl as well as allyl groups, were obtained indirectly by first preparing saturated alkyl ethers of starch of any desired degree of substitution and then allylating these compounds. Some of the alkyl-allyl starch ethers have an advantage over straight allyl ethers in being soluble in the cheap petroleum solvents.

STARCH IN SPONGE FORM HAS POTENTIAL NEW USES

When gelled starch paste, containing about 5 percent of cooked starch, is slowly frozen in a container and then thawed, it becomes—in effect—a sponge saturated with water. If carefully removed by inverting the container, this sponge retains its molded form and much of the water. After most of the absorbed water is removed by pressure, the sponge returns to its original form. If the sponge is dried, it shrinks to about half of its original volume and becomes a hard, somewhat brittle, white, porous solid. If wetted, the dried sponge quickly absorbs about 16 times its weight of water and swells to about twice its original size.

The fact that cooked starch paste can be converted to starch sponge was discovered and reported by a scientist more than a hundred years ago, but apparently no one ever tried to make use of it. Recently, the Northern Regional Research Laboratory has been experimenting with starch sponge with the objective of developing practical uses for it and thus expanding the utilization of starches from domestic plants.

The most promising use for dry starch sponge, which is tasteless but easily digested, is in the manufacture of certain food specialties. Advantage can be taken of its crispness to impart crunchiness to chocolate candies and crackerlike wafers. A new type of confection has been made by saturating and coating bars of dry starch sponge with melted sweet chocolate and allowing them to cool. Such bars, unlike ordinary chocolate bars, remain rigid on hot days. Moreover, the starch sponge has an advantage over popcorn and other puffed cereals, sometimes added to candies to impart crunchiness, in being free from branlike material that irritates sensitive digestive tracts.

Dry starch sponge that has been flavored or made more nutritious by incorporating other material, such as chocolate, flavoring extract, vitamin preparation, fruit, vegetable or meat concentrate, or a protein meal, in the starch paste before it gels and is frozen may be shredded and used like grated coconut or chopped nut kernels. When finely ground, unmodified starch sponge may be used as a stabilizer in candy coatings and cake icings.

Certain mechanical uses for dry starch sponge also seem possible, since it has very low weight per unit volume—about like that of balsa wood—and has high heat-insulating value, together with considerable resistance to crushing.

ENZYME RESEARCH SHOWS HOW TO ALLEVIATE SHORTAGE OF MALT

Experiments by the Enzyme Research Laboratory showed that the addition of extra beta-amylase to western barley malt, which has low diastatic value, brings its diastatic value quite up to that of eastern barley malt. Two cheap plant sources of beta-amylase are wheat flour and sweetpotato juice. This enzyme was prepared from sweetpotatoes in the pure form. The same enzyme may be liberated from wheat flour by treating it with dilute sulphite solution as described in the report for 1943. The enzyme solution thus obtained should be added to the water with which the low-grade malt is to be extracted. The press juice from sweetpotatoes, which is a by-product of sweetpotato starch or dried sweetpotato feed and contains only the water-soluble components of the sweetpotato, may be added instead. Both schemes show promise of helping to alleviate any shortage of distillers' malt by making it possible to get satisfactory results with malt produced from western barley.

The 1944 report stated that raw starch was digested rapidly by a mixture of enzymes from hog pancreas and moldy bran to give a greater yield of fermentable sugars than was obtained with cooked starch by the usual enzymic methods. Further study of this reaction has shown that the efficiency of the mixture of enzymes used is due to the presence of a maltase that aids the starch-splitting enzyme amylase by clearing away the products of starch digestion (principally maltose) as soon as formed, thus permitting the starch splitting to go on faster and more completely. This was shown very clearly by the new observation that only a starch-splitting enzyme, the so-called alpha-amylase of the pancreas gland (frequently a slaughter-house waste), is necessary, provided the split products of the digestion are removed by physical means such as dialysis. The discovery shows promise of application in cases where it is desired to get rid of starch from a product that should not be heated.

FERMENTABLE SUGARS MADE FROM CROP WASTES

The possibility of making fermentable sugars by the acid hydrolysis of cellulose, as well as of starch, has been known by chemists for many years, but the industrial practicability and commercial feasibility of producing a solution of yeast-fermentable sugars from the cellulose in lignocellulose crop residues and, at the same time, utilizing the hemicellulose and lignin components have never been demonstrated.

Experiments at the Northern Regional Research Laboratory, looking toward the utilization of agricultural residues as sources of liquid motor fuels, led to the development, on a laboratory scale, of a continuous two-stage process for converting the cellulose of such materials into a solution of dextrose and the hemicellulose (principally xylan) into a solution of xylose and furfural, leaving the lignin as an insoluable residue. In the first stage, about 95 percent of the xylan is converted by treatment with dilute sulfuric acid into xylose and a

small quantity of furfural. In the second stage, the cellulose is converted into dextrose by a novel procedure that includes impregnation of the dried material with concentrated sulfuric acid at a low temperature. The conversion is accomplished in from 1 to 2 percent of the time and with less than 25 percent of the acid required by other known concentrated-acid processes.

The xylose in solution can be converted by known chemical processes into furfural, an important material for chemical industries. Or, after the small quantity of furfural in the original xylose solution is removed and the solution is neutralized with lime and filtered, the xylose can be recovered in crystalline form or mixed with dextrose and converted by bacterial fermentatiton into butyl alcohol and acetone.

The dextrose solution resulting from digestion of the acid-impregmated cellulosic material with water, after being filtered, neutralized with lime, and again filtered, can be fermented with yeast into ethyl alcohol. Crystallization of the dextrose may offer commercial possibilities.

The conditions for obtaining best results and the yields of products were found to be similar for five agricultural residues—corncobs, sugarcane bagasse, flax shives, oat hulls, and cottonseed hulls. A report of the results obtained in laboratory experiments with corncobs was published in the January 1945 issue of Industrial and Engineering Chemistry.

This process was recommended by the Bureau and the Department for further trial on a semiworks scale as a part of the program for the development of synthetic liquid fuels from nonpetroleum sources authorized by the 78th Congress under Public Law 290, April 5, 1944. As a result, an allotment of $410,000 was made by the Secretary of the Interior, who was made responsible for the research program, to the Secretary of Agriculture for research on the saccharification of agricultural residues for use in the manufacture of liquid fuels.

On November 1, 1944, a separate project, entitled "Synthetic Liquid Fuels Investigations," was set up to carry out this research under the direction of the Chief of the Bureau of Agricultural and Industrial Chemistry. The Chief of the Agricultural Residues Division was designated as a consultant to collaborate with the chemical engineer selected to head this project. The Northern Regional Laboratory had already prepared tentative designs for the equipment required in a semiworks operation capable of producing 2,000 pounds of dextrose in 10-percent solution, 1,600 pounds of xylose in 15-percent solution, 200 pounds of furfural, and 1,000 pounds of lignin residue from 3.3 tons of corncobs in an 8-hour day. On the basis of these designs, plans were made for the construction of a two-story building, 44 by 66 feet, on the grounds of the Regional Laboratory in Peoria, Ill. It was expected that construction would start in the summer of 1945 and be completed early in 1946. Installation of equipment may require an additional 6 months, so it is not likely that the experimental work will get under way before July 1, 1946.

In close cooperation with this special semiworks evaluation project, further laboratory and pilot-plant studies are being carried out by the Northern Regional Laboratory on the development of new and

more extensive industrial uses for lignin and furfural, especially in plastics. The ability of agricultural residues to compete with other materials as sources of synthetic liquid motor fuels is believed to hinge on the profitable disposal of the byproducts furfural and lignin.

CROP RESIDUES SUPPLEMENT STRAW FOR FIBERBOARD

The Northern Regional Research Laboratory assisted the strawboard industry in developing methods for pulping soybean stalks, barley and rice straws, sugarcane bagasse, and certain wild grains, as supplements for wheat straw, and supplied information bearing upon the problems of collection and methods of preserving and storing such raw materials. Because of a lack of farm equipment and shortage of farm labor, some of the strawboard mills have had difficulty in getting sufficient wheat straw. Therefore, during the past year, about 50,000 tons of soybean stalks, the byproduct of soybeans grown for seed, were used as a supplement for wheat straw, together with approximately 50,000 tons of rice straw, 10,000 tons each of barley, rye, and oat straws and smaller amounts of sugarcane bagasse, cornstalks, and flax shives.

About 700,000 tons of wheat straw are consumed annually in the 28 strawboard mills that are scattered over the wheat-growing areas of the United States. The production of flat fiberboard for containers and of corrugated fiberboard for use in packaging has always been an important industry and was even more important during the war emergency. Straw pulp is recognized as being the best low-priced material for making corrugated board for packaging.

SOYBEAN AND LINSEED OILS IMPROVED FOR INDUSTRIAL USES

Oils used in making paints, varnishes, linoleum, oilcloth, and certain rubber substitutes and plastics are useful for these products because they contain esters of unsaturated fatty acids. These unsaturated compounds react with oxygen of the air or among themselves by condensation or polymerization (multiplication of the original molecular weight) to form resinlike or rubberlike solids. The higher the degree of unsaturation (as indicated by the number of double bonds in its structural formula), the more reactive is such a compound, because something can be added at each point of unsaturation. For example, linoleic acid, having two double bonds, "drys" (oxidizes or polymerizes) more rapidly than oleic acid, having one double bond; and linolenic acid, having three double bonds, drys more rapidly than linoleic acid. Linseed oil drys faster than soybean oil because the principal fatty acid in the former is linolenic, while the principal fatty acid in the latter is linoleic. Then, too, some oils contain a fatty acid that has two or more double bonds attached to adjacent carbon atoms, an arrangement technically described as "conjugated." Such oils dry faster than oils containing a fatty acid having the same number of double bonds attached to carbon atoms that are separated by other carbon atoms. Tung oil and chemically dehydrated castor oil, which have exceptional drying or polymerizing power, contain fatty acids that are characterized by two or three conjugated double bonds.

For the last 4 years, some of the Bureau's research on utilization of semidrying and drying oils, as typified by soybean oil and linseed

oil, respectively, has been directed toward the improvement of such oils by processing to conjugate the double bonds of the linoleic and linolenic acid radicals in their component glycerides, or toward the production of superior synthetic drying oils and other products from these fatty acids after being separated from the original oils and conjugated. Extensive experiments at the Northern Regional Research Laboratory have shown that high proportions of the linoleic and linolenic acids in vegetable oils can be converted to their conjugated isomers, without decomposition of the oils, if the oils are heated for definite periods and at definite temperatures with a suitable catalyst. The best catalyst found thus far is nickel on carbon black, which can be prepared by precipitation of nickel oxide on the carbon or by heat decomposition at 360° C. of nickel formate or nitrate on the carbon. Certain special brands of commercial carbon black are suitable.

The results of recent laboratory experiments indicated that the conjugated oils can be heat-polymerized (bodied) to the same viscosities as can the alkali-refined oils, but without the substantial loss of oil and increase in acid value that occur with the latter. When heated to 590° F. (310° C.), a suitable temperature for making bodied oil, conjugated soybean oil polymerizes two to three times as fast, and conjugated linseed oil three to five times as fast, as the corresponding alkali-refined oil.

Paints made with conjugated soybean oil set to the touch two to three times as fast as those made with alkali-refined soybean oil. Under certain conditions of exposure, they were inclined to remain slightly sticky, and therefore to pick up dust, but there is evidence that this objectionable feature can be eliminated by proper control of conditions during the isomerization and by proper selection of drier and pigments.

The conjugated oil, being somewhat more viscous, does not penetrate porous surfaces as rapidly or to such a large extent as alkali-refined oil, and is therefore believed to be more suitable for use in primer coats designed to stop "suction" (oil absorption). Its viscosity, however, is not so great as to make the brush drag when the paint is applied, an objectionable feature of priming paints made with heavy-bodied oil.

Small samples of conjugated soybean and linseed oils were supplied to manufacturers for experimental use in making varnishes, oilcloth, alkyd resins, and other products. Some firms reported good results, and one said it could use large quantities of conjugated linseed oil for a particular purpose if it were available.

The laboratory work carried on thus far has indicated that the products obtained by catalytic isomerization of soybean and linseed oils might have special industrial uses that warrant further investigation. It is planned, therefore, to supply propective consumers with adequate samples for evaluation. Since the substitution of such oils for oils now in use will necessitate changes in formulation and processing, and the peculiarities of the new oils and the relation of these peculiarities to their use must first be determined, it will require considerable time for their introduction. It has already been shown, in the case of chemically dehydrated castor oil, that the establishment

of a new oil in the paint and varnish manufacturing industry may require several years after the process of making the oil has been perfected.

SOYBEAN MEAL USED WITH PHENOLIC RESIN FOR PLYWOOD ADHESIVES

Although soybean meal had been used for many years in making an adhesive for plywood, its use for this purpose declined during the war years because of the demand for waterproof plywood for constructing aircraft and special types of naval equipment. Plywood bonded with soybean glue was considered to be water-resistant but not waterproof; hence, it was displaced to a large extent by plywood bonded with phenol-formaldehyde and other resins.

The annual report for 1944 told how the Northern Regional Research Laboratory had succeeded in developing a new soybean-modified, phenol-formaldehyde adhesive for waterproof plywood, the product consisting of a solvent-extracted soybean meal freed of its water-soluble constituents and mixed with commercially available or freshly prepared phenolic resin in the intermediate stage. A commercial trial had demonstrated that excellent birch and birch-basswood plywood could be fabricated with such an adhesive.

During the past year a plywood manufacturer made practical use of this discovery and consumed half-a-million pounds of a commercial brand of soybean meal, within a 12-month period, in making waterproof plywood. Also, a manufacturer of soybean meal offered to supply large quantities of meal of the proper quality to companies that might become interested in the use of the soybean-modified, phenolic-resin plywood adhesive. So there seems to be a good prospect for increased industrial utilization of soybean meal in adhesives.

Since the new adhesive costs less than other waterproof adhesives and yields plywood that is suitable for use as such, or as concrete-pouring forms, in building houses and other structures, it should help to reduce the cost of construction on farms and elsewhere in the postwar period.

PLASTICS FROM DEXTROSE SUGAR VIA ITACONIC ACID

Up to the present time, itaconic acid has had little application in making plastics, although it is known that when its esters are mixed with acrylates or methacrylates to the extent of 20 to 40 percent, the clear, colorless plastic obtained by polymerization is much harder and stronger than the usual acrylate and methacrylate plastics and, therefore, more suitable for transparent enclosures for airplane pilots, gunners, and bombardiers. High cost of production (requiring a selling price of about $10 per pound) has retarded the use of this valuable material, but there is now a possibility that it can be produced at a cost of 50 cents or less per pound by a mold-fermentation process developed by the Northern Regional Research Laboratory.

In this process itaconic acid is produced by a strain of *Aspergillus terreus* cultured on a 20-percent solution of dextrose (made from cornstarch). The supplemental nutrients required by the mold in sub-

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merged culture were found to be entirely different from those required in surface culture. The conditions contributing to high yields of itaconic acid were determined for both types of culture in laboratory equipment. In the surface-fermentation studies the maximum production of itaconic acid was 37 grams per 100 grams of dextrose supplied, and the maximum recovery of the acid was 33 grams per 100 grams of dextrose. With submerged cultures, as represented by fermentation in shaken flasks, the maximum production of itaconic acid was 25 grams per 100 grams of dextrose supplied.

By surface culture, it should be possible to produce itaconic acid at a cost of 40 to 50 cents a pound in plants equipped with large shallow pans, and if the yield by submerged culture can be further improved, as seems likely, it may be possible to produce it at a cost of less than 40 cents a pound. Even at the higher cost and appropriate selling price, itaconic acid would undoubtedly be in demand for making transparent plastics. At the lower cost of production and proportionate selling price, it might also find application in manufacturing a special type of detergent for which it is potentially useful.

VULCANIZING RECIPES DEVELOPED FOR ACRYLIC "RUBBERS"

Further advances have been made at the Eastern Regional Research Laboratory in the preparation of elastomers from acrylates derived from lactic acid. The vulcanizing or curing characteristics of three types of acrylic "rubbers" (lactoprenes) have been studied extensively. The first type, consisting of polyacrylic esters, can be cured with para-quinone dioxime and red lead, benzoyl peroxide, dichloroquinonechloroimide and litharge, or other oxidizing agents. Milling with chlorinating agents makes such material vulcanizable by sulfur and accelerators. The second type, acrylic copolymers containing a small proportion of unsaturated compounds, can be cured with the agents just mentioned and also, without prior chlorination, by recipes containing sulfur and accelerators. The third type, saturated copolymers of acrylic esters containing 5 to 10 percent of a reactive compound (such as chloropropyl acrylate, acrylonitrile, phenyl acrylate, or cyanoethyl acrylate), permits the widest selection of vulcanizing recipes such as used with natural or synthetic rubbers. The recipe to be used for vulcanization should be selected on the basis of the reactivity of the copolymer. A change in recipes often produces greater differences in the rate of vulcanization and in the properties of the vulcanizates than the use of different copolymers.

The vulcanizates are resistant to oils, oxidation, sunlight, and heat. They have excellent cut-growth resistance. By the proper choice of recipes, vulcanizates of outstanding resistance to heat aging or having low permanent set or a wide variation in tear strength can be prepared. These acrylic "rubbers" may also be compounded for use as latex or cement.

Through the use of different types of lactoprene and a variety of vulcanizing agents, many types of rubberlike products can be obtained. These appear to have possibilities for the manufacture of various kinds of articles for special uses.

CASEIN SEPARATED INTO TWO FRACTIONS

Proteins generally occur as mixtures, and casein from milk, although once regarded as a single substance, is no exception. In view of the wide industrial importance of casein and its potential availability, the Eastern Regional Research Laboratory started an investigation of its components. After many procedures were tried and discarded as not feasible, it was found that advantage could be taken of the small difference in isoelectric points of the alpha and beta components. The alpha-casein was precipitated at low temperature by approaching the isoelectric point from the acid side, while the beta-casein remained in solution. Several fractionations yielded the alpha and beta components entirely free from each other. Recombined in the ratio of about 4 to 1, as they occur in skim milk, they gave the same electrophoretic pattern as the original unfractionated casein. Alpha-casein, which constitutes about 80 percent of the crude protein, contains a greater amount of acidic phosphoric acid groups and migrates more rapidly in the electric field than does the beta-casein. Although physical measurements had previously indicated that casein is a mixture, this is the first time that its components have actually been isolated. So far, only small quantities have been prepared for laboratory investigations of their useful properties.

CASEIN BRISTLES MAY FIND INDUSTRIAL MARKET

A number of brush manufacturers have shown interest in casein bristle, mentioned in the report for 1943, and two companies have retained consultants to appraise its manufacturing possibilities. One of these consultants has been operating a pilot plant with cooperation of the Eastern Regional Research Laboratory. For commercial production, it is desirable to use a continuous process rather than an intermittent one. Consequently, in this pilot plant, the piston extruder first employed in the laboratory experiments has been replaced by a continuous screw extruder. The quality of the fiber is the same, but the screw extruder is more convenient and permits a greater production. Other units have been designed for continuous stretching and hardening and are being subjected to trial runs. Among these is a new type of self-advancing reel.

The problem of finding suitable materials for imbedding casein bristle in paint brushes has been given considerable attention. A mixture of urea-formaldehyde with an alkyd resin has proved particularly satisfactory in giving a solvent-resistant setting.

There appears to be an excellent future market for bristle material, and it is estimated that casein bristle can be produced at a markedly lower cost than that of natural bristle or other competing artificial bristle.

RESEARCH ON FIBERS-FROM-FEATHERS PROBLEM MAKES PROGRESS

Feathers are similar to hair and wool in chemical composition and would make good artificial fibers if it were possible to change the form without sacrificing any of the desirable properties of their principal component, keratin protein. Thus far, it has not been possible

to disperse keratin into a spinnable liquid without breaking the disulfide bonds characteristic of this protein and apparently responsible for its chemical and physical stability. Spinnable dispersions have been prepared at the Western Regional Research Laboratory by treating feather keratin with a slightly alkaline solution containing a reducing agent and a commercial wetting agent or detergent of the alkyl-aryl sulfonate type, as mentioned in the 1943 report in connection with new uses for proteins, and more recently by heating a suspension of feathers in water containing propylene oxide, whereby the keratin becomes partly soluble in certain organic solvents. After the filaments are spun from dispersions prepared in either way, the protein part of the complex can be released or regenerated, but not in its original condition and with its original properties, since the disulfide bonds cannot be restored.

The filaments from dispersions prepared under these relatively mild conditions are much better, however, than those from dispersions prepared under severe conditions, such as by ball milling or by treatment with strongly alkaline solutions. When properly handled they have considerable elasticity, flexibility, and tensile strength when dry. They are softened and weakened by wetting. However, the wet strength of modified keratin filaments has been materially increased—sometimes doubled—by treating them with formaldehyde or with the isocyanates of certain aliphatic or aromatic alcohols.

PENICILLIN YIELDS INCREASED THROUGH RESEARCH

Penicillin production increased from 13 billion units in January 1944 to 394 billion units in January 1945, and reached 647 billion units per month in June 1945. This expansion in production did not result from increased manufacturing facilities, but rather from a combination of better operating conditions and better molds. The latter were developed through research by members of the industry itself, through projects under the auspices of the Office of Production Research and Development of the War Production Board, and by the Northern Regional Research Laboratory.

Numerous experiments were made at the Northern Regional Laboratory to determine the effects of variations in each of the many factors that control penicillin yields by different organisms in different types of fermentation equipment. During some of the fermentations, periodic analyses were made of the medium and the fermentation products. From the results has come a partial understanding of the chemical changes taking place in the medium while penicillin is being produced, which made it possible to delineate improved operating conditions for the attainment of higher yields.

In the laboratory fermentations it was possible, with improved organisms and improved operation, to obtain yields of 300 units per milliliter in small quiescent surface cultures, 200 units in shaken flasks, and up to 450 units in rotating drums and a large pilot-plant vat fermenter. The best yields previously obtained in submerged cultures were from 150 to 175 units per milliliter.

Last year's report stated that the newly discovered organism NRRL 1951.B25, a strain of *Penicillium chrysogenum* isolated from a moldy cantaloup, was markedly superior as a penicillin producer to the two

organisms then in general commercial use, which were NRRL 1249.-B21, an improved descendant of the original Fleming strain of *Penicillium notatum* for surface fermentations, and NRRL 832, the best of several distinct strains of *P. notatum* from the laboratory's own culture collection for deep fermentations.

The best organism for the production of penicillin in submerged cultures, and the one giving the highest yield obtained thus far by any method, is an X-ray mutant derived by the Carnegie Institute (Cold Spring Harbor, New York) from NRRL 1951.B25 in research conducted under the auspices of the Office of Production Research and Development. This organism, known as X–1612, has produced 450 units of penicillin per milliliter in experiments at the Northern Regional Laboratory. If the recovery problem or some other difficulty does not interfere with the general industrial adoption of X–1612, a further marked increase will occur in penicillin production without any increase in manufacturing facilities. The tremendous value of a better mold strain cannot be overemphasized. With apparent penicillin production in 1945 of approximately 8,500 billion units, which will sell for about 60 million dollars, an organism that can increase production by only 10 percent without additional cost would be worth 6 million dollars a year.

Another of the improved organisms, NRRL 1984.A, is a strain selected by the Northern Regional Laboratory from a culture of *P. chrysogenum* isolated at the University of Minnesota. It produces a very high yield of penicillin in submerged culture, and a substantial proportion of the product is Penicillin X, a partciular form of penicillin having unusual, interesting, and possibly important properties, which was discovered last year at the Northern Regional Laboratory through cooperation with industrial penicilllin producers.

ANTIBIOTICS RESEARCH YIELDS NEW FACTS

Research on several antibiotics, other than penicillin, was carried out by the Western Regional Research Laboratory, the Pharmacological Laboratory, and a new division, recently organized for basic research under the Bankhead-Jones Act of June 29, 1935, on biologically active chemical components of plants in cooperation with the United States Bureau of Plant Industry, Soils, and Agricultural Engineering, at Beltsville, Md.

The work at Beltsville began in a small way in October and gained momentum as the professional staff increased from one to three persons. One of its broad objectives is to isolate and identify biologically active compounds from green plants with particular reference to compounds possessing antibiotic activity toward micro-organisms that cause plant diseases. Attention was first directed toward tomato plants of varieties possessing moderate and marked resistance to fusarium wilt and other varieties that are susceptible to this disease. Fractionation and concentration of the juice pressed from wilt-resistant tomato plants yielded a crude preparation which, in laboratory tests, showed marked ability to inhibit the growth of the *Fusarium* fungus responsible for wilt. The antibiotic substance in this preparation was named "tomatin." It occurs throughout the tomato plant, but its concentration varies somewhat with the age of the plant and considerably with the plant part assayed.

Some of the physical and chemical characteristics of tomatin were determined, and a satisfactory method was developed for determining the relative abilities of different preparations containing this substance to inhibit the growth of the tomato-wilt fungus in a culture medium. This method, patterned after the cylinder-plate method for the assay of penicillin, was described in a paper prepared for publication. Sufficient data have not been obtained as yet to justify definite conclusions as to the relative amounts of tomatin in the samples assayed or a quantitative relationship between the concentration of this substance and the occurrence of wilt in tomato plants. Efforts will be made to purify the crude antibiotic preparation and eventually to isolate and characterize tomatin and to determine its specificity with regard to the tomato-wilt organism.

At the Western Regional Laboratory attention has been given to lysozyme, a bacteria-destroying enzyme contained in egg whites, and to antibiotic substances produced by certain micro-organisms that might be grown on media prepared from vegetable wastes, such as asparagus butts. These antibiotics include: citrinin, produced by *Penicillium citrinum;* subtilin, produced by *Bacillus subtilis;* tyrothricin, a complex substance produced by *Bacillus brevis;* and gramicidin, one of its constituents.

A simplified procedure for preparing pure crystalline lysozyme was developed and used regularly in the laboratory for obtaining enough lysozyme for use in research. It is believed that this procedure can be adapted to commercial use and that, if lysozyme is found to be useful in therapeutics or as a food preservative, the simplified method will make the preparation of pure lysozyme from the waste egg white adhering to egg shells at freezing and drying plants both possible and feasible.

The optical and crystallographic properties of lysozyme and some of its salts were determined. Experiments showed conclusively that the bacteria-destroying power of preparations containing lysozyme was due to the specific action of lysozyme itself and was not influenced by the presence or absence of biotin, the powerful vitamin H of egg yolks, or avidin, a biotin-inactivating protein of egg white. The isolation of lysozyme from egg white and the relationship of lysozyme, biotin, and avidin were discussed in papers published in scientific journals.

Extensive experiments with lysozyme in the Pharmacological Laboratory confirmed the results of previous preliminary tests which indicated that laboratory animals sensitized with lysozyme suffer fatal anaphylactic shock when lysozyme is subsequently introduced into their blood streams. These results indicate that, unless lysozyme can be modified by chemical treatment to destroy its shock-producing ability, medicinal use as an antibiotic against pathogenic bacteria must be limited to the surface of the body.

Citrinin, a yellow antibiotic substance, was produced by culturing the mold *Penicillium citrinum* on asparagus-juice medium, and was purified by sublimation under reduced pressure and also by extraction with a solvent. The purified substance was used in studies of the physical and physiological properties of citrinin. Studies of its acute toxicity for laboratory animals had been made previously. Additional experiments were made by the Pharmacological Laboratory

to determine its subacute toxicity and to learn how it affects the various structures and functions of animal organs. The results, which have been published, give the first complete picture of the pharmacological properties and toxicity data for this antibiotic, which has been known since 1931. Studies on rate of excretion and maintenance of concentration of the drug in the blood remain to be investigated. The correlation of the new and previously acquired data with the known effects of citrinin on pathogenic organisms will permit the final evaluation of this antibiotic as a potential therapeutic agent.

The properties of subtilin, an antibiotic discovered and named by the Western Regional Laboratory in 1943, and the conditions for culturing *Bacillus subtilis* for the production of subtilin were described in a paper published in the July 1944 issue of the journal Archives of Biochemistry. The discovery that subtilin in solution can pass through a membrane of transparent cellulose and thus be separated from colloidal substances led to a modification of the method of preparing subtilin from the alcoholic extract of the spent culture medium. About the same proportion of subtilin was recovered as in the original procedure (70 percent), but the purified powder obtained by the new method was about three times as active as that obtained by the original method, being effective against *Staphylococcus aureus* when there was 1 part in 2 million parts of water. Apparently, in the original method the subtilin was partly inactivated in the process of purification.

Preliminary experiments by the Pharmacological Laboratory on the acute toxicity of a subtilin preparation indicated that a dose of 40 milligrams or more of subtilin per 1,000 grams of body weight would kill a white rat. The results emphasized the need for more extensive studies on the acute and subacute toxicities of subtilin to determine whether toxicity will increase or decrease as impurities are removed. Regardless of subtilin's effectiveness against certain pathogenic organisms, its use as a drug will depend on the results of thorough pharmacological studies.

The antibiotic tyrothricin is being produced commercially for external use by physicians and veterinarians against certain microbial infections. Previous work at the Western Regional Laboratory showed that it can be produced in yields that are higher than usual when a juice concentrate made from asparagus butts is used as the culture medium. During the fiscal year a paper based on this work was prepared for publication in a scientific journal; it discussed the factors that promote high yields of tyrothricin in shallow-layer cultures and the use of juice concentrates from waste asparagus butts as culture media without the addition of other nutrients.

The use of tyrothricin is limited by its high toxicity to animals, one of its effects being to destroy red blood corpuscles. It can be fractioned into two distinct antibiotics, tyrocidin and gramicidin. Both of these are effective as antibiotics in test-tube trials, but only gramicidin is considered to be effective in the presence of body fluids and tissues. The use of gramicidin is limited because, like the mixture, it is toxic and destroys blood corpuscles.

In efforts to reduce the toxicity of tyrothricin and gramicidin, it was found that treatment of a solution in alcohol with formaldehyde and alkali yielded products that were only 10 to 20 percent as destruc-

tive to blood corpuscles as were the original substances. In the case of the modified tyrothricin, the antibiotic activity against *Staphylococcus aureus* was reduced, but in the case of modified gramicidin it was retained. Preliminary tests by interperitoneal injection indicated that the modified gramicidin is considerably less toxic to rats than is the unmodified substance. Because the modified gramicidin promises to be useful as a chemotherapeutic agent, a brief paper announcing the discovery of this product and describing its preparation was prepared for publication in a scientific journal. Further and more detailed studies of the chemical and biological properties of modified gramicidin are in progress.

RUTIN EXTRACTED COMMERCIALLY FROM BUCKWHEAT PLANTS

Significant progress was made in developing new sources of rutin and improving the process for extracting it for medicinal use. Green buckwheat plants were found to contain comparatively large quantities of rutin which can be extracted by a simple process and with such equipment as is usually employed in pharmaceutical manufacturing. The result has been a considerable lowering of the cost of rutin. When rutin is prepared from high-quality, flue-cured tobacco, which contains about 0.4 percent of this glucoside, the material cost is $135 to $150 per pound of rutin. By using buckwheat, which contains 3 to 5 percent of rutin, the material cost is reduced to $0.87 to $1.10 per pound. Rutin may be prepared from either green or dried buckwheat.

The green plant, harvested with a binder, is placed in a vat and extracted with alcohol, after which the extract is recovered by percolation. When the alcohol has been evaporated from the percolate crude rutin separates from the watery residue on standing. This is collected and freed from fatty impurities by washing with benzene. The rutin is recrystallized from boiling water, treated with silica gel to remove impurities, and again recrystallized from boiling water. The product is then of medicinal purity.

Slow drying of buckwheat results in considerable loss of rutin. Therefore a quick drying and stem eliminating procedure was developed; this produces a dry meal of leaves and blossoms that can be stored for future extraction. Rutin is obtained from this dried buckwheat meal in the same manner as from the green plant.

While the percentage of rutin in buckwheat is highest when the plant is in full bloom and before any seeds are set, the greatest yield per acre is obtained two or three weeks later due to rapid growth of the plant. The leaves contain the largest percentage of rutin; the blossoms, about half as much; the stems, still less; and the ripe seeds, none.

During the summer of 1944, the Eastern Regional Research Laboratory prepared approximately 20 pounds of pure rutin, a larger quantity than had ever existed previously. Several drug manufacturers planned to begin the commercial production of rutin in 1945.

Over one hundred physicians and pharmacologists collaborated in clinical studies on rutin, and several hundred patients were treated. The clinical evidence continued to confirm the effectiveness of rutin in reducing increased capillary fragility to normal and, where it is

associated with hypertension, to prevent retinal hemorrhage and cerebral accidents. Evidence was also obtained that rutin prevents capillary rupture from the use of thiocyanates and other drugs.

GLUTEN SULFATE AROUSES INTEREST AND IS MADE BY IMPROVED PROCESS

In the annual report for 1943 brief mention was made, in connection with the utilization of wheat by chemical industries, of a sulfate derivative of gluten which, upon contact with water, absorbs about 200 times its own weight of the water and changes from a powder to an irreversible gel. Because of its exceptionally high absorptive power, this product was believed to be promising as a surgical dressing to accelerate the healing of wounds. Following the publication of a paper describing the preparation and properties of gluten sulfate, requests were received from about 60 correspondents for further information and samples. Later requests were received from some of the same correspondents for larger samples and information concerning regular supplies. One company wanted to purchase 500 to 1,000 pounds. From these facts, it appears that gluten sulfate has been found useful for certain purposes and may eventually become a commercial product.

Further investigation on the preparation of gluten sulfate resulted in the development of a simpler and less costly process and yielded fundamental knowledge regarding the nature of the reaction. The original process for making gluten sulfate with chlorosulfonic acid is covered by a public-service patent (No. 2,344,267). The improved process involves the treatment of wheat gluten with concentrated sulfuric acid at a very low temperature (–30° F.).

ALLERGENS OF EGGS AND CASTOR-BEANS INVESTIGATED

Data accumulated by the Allergens Research Division in the study of both commercial and experimental chick-embryo vaccines in collaboration with the Army Medical School have led to the identification of egg and embryo-tissue antigens in these preparations and also to the detection of other antigens of possible significance. These antigens are native proteins of the egg or embryo tissue. They contribute nothing to the protective value of the vaccine. Advantages to be gained if these unwanted proteins can be excluded from chick-embryo vaccines have been impressively demonstrated by the deleterious effect of the proteins—anaphylactic shock, death, and invalidation of serological tests. The problem of exclusion of these proteins is clearly outlined in available data. It is now reasonable to anticipate that the solution of this problem will depend on coordinated study of the chemical and immunological properties of the native proteins of normal and embryonated eggs.

Evidence secured from recent studies of oilseed allergens represented by the 1A fraction of castor-bean indicates that the allergenic component is composed of more than two—perhaps several—distinguishable compounds. These are closely related to each other with respect to chemical composition, and for that reason they are difficult to separate in homogeneous form. Fortunately, the allergenic com-

ponents of the 1A fraction apparently possess a high degree of stability, as shown by maintenance of allergenic and other immunologic properties after exposure to rigorous treatment in successive stages of fractionation.

EGG POWDER FURTHER IMPROVED THROUGH BACTERIOLOGICAL AND CHEMICAL STUDIES

The quality of whole-egg powder and retention of quality during storage have been further improved through bacteriological and chemical investigations on spray-dried eggs. From the knowledge gained thus far, and from what may be reasonably expected of investigations still in progress, it is believed that egg powder, like milk powder, will become a generally accepted food product in the postwar era for home, institutional, restaurant, and bakery trade uses.

The Microbiology Research Division has examined over 6,000 samples of egg powder which were submitted by 100 dehydration plants, has undertaken studies in plants, and has engaged in cooperative research on samples prepared or selected to show the effects of different processing methods, moisture contents, storage temperatures, and sanitary measures. Data acquired by the Division were supplied to Government agencies responsible for the purchase of egg powder for the military forces and lend-lease shipments.

These data, and suggestions based upon them, were helpful in the preparation of the War Food Administration's 1945 purchase specifications for egg powder and minimum tentative requirements for facilities, operating procedures, and sanitation in egg-breaking and egg-drying plants. They were also helpful in enabling the egg dehydration industry to make a more scientific approach toward the selection of better-quality raw material, toward improvement in plant sanitation, processing, handling, and storage methods, and, in consequence, to the production of egg powder of higher microbiological quality.

The 1944 production of dehydrated egg amounted to over 300,000,000 pounds. Large-scale production still continues. If present knowledge is applied to processing, it is not likely that the future of the industry will be endangered because of the poor microbiological quality of the egg powder produced. However, microbiological problems still remain to be solved before the consuming public can be assured of the very best powder possible.

Fundamental research on the chemical changes that take place in egg powder during storage, how these changes affect consumer acceptance, and how the quality is influenced by variations in the conditions of preparing, packaging, and storing the product, was carried on by four divisions of the Western Regional Research Laboratory in cooperation with the Quartermaster Corps of the United States Army.

Through extensive experiments on egg whites and egg yolks dried separately in a vacuum from the frozen state (a process known as lyophilization) and on mixtures of the dried egg white and egg yolk, in comparison with dried whole egg, it was found that the deterioration in quality, as represented by palatability, results from chemical changes in the egg-yolk constituents. Further experiments on the four fractions of the yolk, separated by physical methods (without heating) to avoid chemical changes, indicated that the changes principally responsible for the development of off-flavor take place in the

phospholipids (fatlike esters of phosphoric acid) and the glycerides (true fats), and that they result from oxidation.

Measurement of the degree of fluorescence of a solution prepared by extracting egg powder with 10-percent potassium chloride solution is used by Government purchasing agents as an indication of the extent of chemical changes in egg proteins during processing or storage, and there is a tendency to use this test as a substitute for actual tasting of the product. Studies at the Western Regional Laboratory have shown that a brown substance possessing fluorescence is formed in egg powder under the usual conditions of storage and is probably due to a reaction of certain nitrogen compounds (amines) in both the white and yolk with glucose, which is a natural minor constituent, or with aldehydes, which may be formed by the oxidation of unsaturated fatty-acid groups. The formation of this brown substance, which discolors the powder and makes it less acceptable to consumers basing their choice on appearance, is not necessarily related to the development of off-flavor. Therefore, reliance on the fluorescence measurement as a substitute for flavor-score evaluation by a tasting panel does not appear to be warranted.

It was found that the development of fluorescent substance soluble in 10-percent potassium chloride solution is dependent on the presence of moisture to a greater degree than is the development of off-flavors. The moisture content of egg powder permitted under 1945 specifications for Government purchases was 2 percent or less, which is less conducive to the formation of fluorescent substance than was the 4-percent moisture formerly allowed.

Preliminary investigations on the advantages of displacing the air in cans of egg powder with low-oxygen gas indicated that packaging in carbon dioxide, in nitrogen, or in a mixture of these two gases may considerably extend the shelf life of egg powders under the severe conditions incident to military use. In laboratory experiments the addition of a little acid to the egg mixture (to pH 5.5) before dehydration retarded the development of off-flavor in the resulting egg powder, but this practice has not been developed to the point where it can be recommended for commercial adoption.

Egg powder dried from the frozen state (lyophilized) is not likely to be damaged in processing. Samples of dehydrated eggs prepared in the laboratory by this method permitted studies of deteriorative changes resulting from conditions of packaging and storage, entirely distinct from changes that might result from conditions of processing. The adaptation of this process to commercial use still remains to be worked out.

The chemical investigations carried out thus far have shown that careful dehydration of whole-egg mixture to a low moisture content (below 2 percent), packaging in low-oxygen gas, and slight acidification of the egg mixture before drying it, materially extend the shelf life of high-grade egg powders.

DEHYDRATED VEGETABLES IMPROVED IN QUALITY AND STORAGE LIFE

Better quality and a longer shelf life for some of the more important dehydrated vegetables have been made possible by this year's research at the Western Regional Research Laboratory on scientific and tech-

nological problems of the dehydration industry. Extensive experiments were made to learn how to make good dehydrated vegetables retain their color and flavor, as well as their nutritive qualities, under the most extreme storage conditions, that is, at temperatures of 90 to 120 degrees Fahrenheit.

Treatment with a solution of sulfur dioxide or sodium sulfite before dehydration, which had previously been found beneficial in the case of cabbage, also improved the keeping qualities of dehydrated carrots and potatoes, when these were stored at high temperatures. A solution of sulfur dioxide is better than one of sodium sulfite for treating potatoes and carrots, because the sodium fraction of the sodium sulfite tends to make the product mushy when rehydrated for cooking.

Storage experiments at high teperatures were made on sulfited and unsulfited potatoes and carrots, and on sulfited cabbage, in 5-gallon sealed metal cans, in some of which the air was displaced with nitrogen containing 1.5 percent of oxygen. Each of the vegetables was dehydrated to three different moisture levels before packaging; one lot contained the amount of moisture permitted under current government specifications; another lot contained 1 to 2 percent more moisture; and another contained 1 to 2 percent less moisture. At the same time, some of each vegetable, dried to the specified moisture content, was sealed in a can together with some granulated calcium oxide in a small moisture-permeable container, which was expected to absorb more moisture from the dehydrated vegetable during the storage period. Thorough testing and analysis of the stored products after various storage periods, up to 3 months, indicated that the samples containing the least moisture were in much the best condition. From the results, it was estimated, for example, that the reduction of moisture content of dehydrated potatoes from 7 percent (allowed by specifications) to 5 percent doubled the storage life of the product, and that the reduction of moisture content from 7 percent to 2 percent, achieved at 120° F. by the use of calcium oxide in the package, increased the storage life of the product sixfold.

The products packed in nitrogen containing 1.5 percent of oxygen were better than those packed in air (containing about 21 percent oxygen). Oxygen within the package of dehydrated vegetable increases the rate of flavor deterioration and also increases the loss of vitamin C and of carotene, the precursor of vitamin A. There is evidence that certain oxidative degradation reactions, notably rancidification of oils, are more rapid in very dry materials. Therefore, if full advantage is to be gained from the use of calcium oxide in the package to reduce moisture to the lowest possible limits, the air in the packed product must be completely displaced with nitrogen.

In order to include the desiccating material in the package of dehydrated vegetable there must be some sacrifice of space. Granulated calcium oxide will absorb moisture equal to 30 percent of its weight to form a dry powder of increased bulk (nearly 1½ pints per pound). With potatoes and carrots, a moisture loss of about 4 percent can be achieved through sacrifice of about 14 percent of the space in a 5-gallon can for 2 pounds of desiccant and its moisture-permeable container. With cabbage, about 3 percent of moisture is lost to 1 pound of desiccant which, with its container, occupies about 7 percent of the available space in a 5-gallon container.

Although a brief blanching (scalding) treatment is usually given to vegetables prior to their dehydration, in order to inactivate certain enzymes that might cause deterioration of the dried product, careful experiments have proved that no advantage is gained by long blanching of potatoes, beets, carrots, and cabbage. Minimum blanching, even though some peroxidase enzyme still remains, results in a better product, especially with regard to texture after rehydration. There are some indications that blanching may be omitted entirely as a preliminary treatment for beets and carrots. In view of these findings, Government purchasing agencies have adopted the Western Regional Laboratory's solution-color test for peroxidase, which provides for a certain tolerance, for use on dehydrated potatoes and have entirely abandoned the peroxidase test on dehydrated beets, which had caused much difficulty.

FROZEN FRUITS IMPROVED AND USED IN NEW PRODUCTS

Research at the Western Regional Research Laboratory on the freezing preservation of fruits has benefited both the commercial growers and the industrial consumers of fruits. In the past few years there has been a tremendous increase in frozen packs of apples, apricots, peaches and cherries. These frozen fruits are used extensively by the baking industry for making pies, because the pies made with quick-frozen fruit are almost as good as those made with fresh fruit.

It has been a common practice to pretreat sliced apples, and other prepared fruits that darken on exposure to air, with sulfur dioxide to inactivate the oxidizing enzyme. Sodium bisulfite solution as a dip can also be used, but it penetrates the fruit more slowly. The Western Regional Laboratory found that this disadvantage of sodium bisulfite solution can be largely overcome by the use of a holding period and by slightly acidifying the solution (to pH3). The use of sodium bisulfite makes the preparation rooms more comfortable by eliminating the irritating fumes of sulfur dioxide. Certain concentrations of bisulfite for use with particular fruits have been recommended to the industry. A method for the determination of sulfur dioxide in fruits, which is particularly adapted to frozen fruits, has been developed.

Frozen fruit puree is rapidly gaining in popularity, because it preserves to a high degree the color, flavor, and nutritive qualities of the fresh fruit. It can be made from any fully ripe, raw fruit that has a decided flavor, and its manufacture makes possible the maximum utilization of a fruit crop for food, since low-grade, odd-sized, misshapen and blemished fruit can be used if it is internally sound and full-flavored, and when the quantity of first-class fresh fruit exceeds market demands, the surplus can be preserved as frozen puree. Frozen fruit purees serve as flavor bases for ice creams, sherbets, ices, and beverages, and they are suitable for the manufacture of jam, Velva Fruit frozen dessert, and frozen jellied fruit, the last two being products recently developed by the Western Regional Laboratory. As a result of the dissemination of information on Velva Fruit through publications, correspondence, and personal contacts, ice cream manufacturers in at least eighteen large southeastern cities of the United States have produced this product commercially. The frozen jellied fruit is made from either freshly prepared or frozen uncooked

fruit purees or fruit juices. This product contains less sugar than the usual types of jellies and jams; its soluble solids content is approximately 56 percent, while that of the usual jellies, jams, and preserves varies from 65 to 68 percent. Since the fruit is not heated, the pectin of the fruit is not extracted; therefore a small amount of rapid-set citrus pectin is included in the formula. The pectin is peptized in the unsweetened puree or juice at room temperature, the sugar is added, and the mixture gels at room temperature before freezing. Since such products are made from raw fruits and insufficient sugar to prevent the growth of molds, it is necessary to freeze them and keep them under refrigeration until used. Formulas are ready for commercial trials.

PECTIN PRODUCTS MADE BY NEW PROCESSES AND USED IN NEW FOOD SPECIALTIES

The practical research on the extraction and utilization of pectin products has been made possible by the fundamental chemical and physical research on pectin. Thus, information that is essential to the development of pectin products having commercial possibilities has been supplied by fundamental research on the physicochemical properties of pectinic acid; also, the study of viscosity characteristics of pectinic acid solutions has aided in the development of a less costly method of preparing low-methyl ester pectinates.

During the past year, a new method of preparing low-methyl ester pectin was developed through the laboratory stage at the Western Regional Research Laboratory. This method must be tried on a pilot-plant scale and found practical before it is recommended for industrial use, but it appears very promising as a means of producing low-methyl ester pectin at a much lower cost than formerly considered possible, since neither vacuum concentration nor the use of alcohol is required.

A United States patent (No. 2,375,376) was granted to two scientists of the Western Regional Laboratory and assigned to the Secretary of Agriculture for a "Method of extracting pectinous materials." This method is adapted particularly to pectinous materials, like citrus fruit skins, whose ash-forming constituents are high in calcium. By its use a higher yield of pectin can be obtained, in a shorter time, than by the usual commercial methods, and the product is of high quality. The novel feature of this method is the addition to the acidified aqueous extracting medium of a chemical compound that forms a soluble complex with calcium and thus releases pectinic acid that would otherwise be retained in the material as insoluble calcium pectinate. An alkali metaphosphate or polyphosphate may be used.

Experiments on the extraction of pectin from apples showed that the protopectin in fresh apple pulp, a byproduct in the manufacture of cloudy-type apple juice, is converted to soluble pectin of high grade during storage in a dilute solution of sulfurous acid for 6 months, after which the pectin extract can be recovered by heating and pressing. This method of solubilizing the pectin content of waste apple pulp provides apple processors with an inexpensive source of a liquid pectin product of high quality for use in making jellies and jams.

Extensive experiments were made on the use of low-methyl ester pectin, obtained by controlled alkali deesterification of pectin, in the production of new food specialties. A powder, which can be mixed with hot water to make a dessert that is similar to gelatin desserts but sets without refrigeration, was formulated and submitted to the Office of the Quartermaster General for consideration as a food item for soldiers in hot climates and other places where there are limited refrigeration facilities. After this powder and a similar product from a commercial firm were examined, tentative specifications were drawn up for the purchase of such material.

A newly developed cold-water pudding mix is also based on the use of low-methyl ester pectinate. It consists of two powders. One, a mixture of low-methyl ester pectinate and sugar, is first dissolved in cold water; then the other, a mixture of powdered whole milk, sugar, salt and dry flavoring material, is added. Upon stirring for 2 or 3 minutes, a paste of smooth consistency is formed, which sets to a gel after standing 3 or 4 minutes. Several large batches of this product have been used with satisfaction by the Ninth Service Command of the United States Army as a dessert item on hospital trains out of San Francisco.

A low-sugar jellied fruit dessert or salad (60 percent fruit and 40 percent jellied sugar sirup) was also prepared by heating the prepared fruit, sugar sirup, and low-methyl ester pectin to sterilizing temperature and packing in airtight cans. The later work on this product was done at the request of representatives of the Quartermaster Corps of the U. S. Army, who thought it had possibilities as a dessert item in Army food rations. As a result of similar recommendations from the Western Regional Laboratory and a commercial firm, the Quartermaster Corps issued Tentative Specification C. Q. D. No. 335 for "Fruit Dessert: Jellied," under which more than 20 million cans had been purchased for use in army field rations before the end of the fiscal year. Because of its superior quality, good storage stability, and relative simplicity of manufacture, this product offers much promise in the postwar food market as a convenient, ready-to-use dessert or salad.

APPLE-FLAVORING CONSTITUENTS OBTAINED IN CONCENTRATED FORM

The Eastern Regional Research Laboratory developed a process for recovering the volatile flavoring constituents of apple juice in the form of an essence. One gallon of the essence contains the volatile flavoring constituents of 100 to 200 gallons of juice. Blending this essence with a good grade of commercial apple-juice concentrate results in a full-flavor concentrate which, with the mere addition of water, becomes a beverage having the taste and aroma of fresh apple juice. The process includes the following steps: (1) Rapid evaporation of about 10 percent of the juice; (2) mechanical separation of the vapors from the unvaporized juice; and (3) fractionation of the vapors to obtain a concentrated flavor or essence.

A mimeographed circular (AIC–63) describes the process, equipment, and costs for large-scale operation. A unit costing approximately $4,000 would have a capacity of 10,000 gallons of juice per

day. Such a unit would produce the essence at a cost of about sixty cents a gallon. The estimate includes amortization and all other costs except that of the juice itself.

In addition to being convenient for preparing beverages, an apple juice concentrate into which apple essence has been incorporated has obvious uses in the preparation of sherbets, ices, and fruit jellies. The essence may also find applications in the preparation of table and candy-coating sirups, by being incorporated with apple sirup or sugar sirups, and in the apple-juice canning industry for the production of a superior product.

Since much of the apple juice evaporated commercially into sirups goes into products for which the natural apple flavor is of no value, the volatile flavoring constituents now discarded in the preparation of these sirups could be obtained in concentrated form by this new process and sold as natural-flavoring essence.

Market surveys, industrial contacts, and reports upon samples have indicated a marked interest on the part of food processors in the production and use of full-flavor juice products, such as can be made with the essence obtained by this new process. At least one large factory was expected to be in operation in the fall of 1945, and several other companies had the necessary equipment under construction.

The flavor recovery process has also been successfully used on the juices of Concord grapes, black raspberries, currants, and strawberries, and indications are that with slight modifications it is applicable to other fruit juices. This new process should make it possible to produce jellies, jams, preserves, and bottled beverages having improved true fruit flavor at a negligible increase in cost.

NORTHWESTERN PEACH GROWERS AND CANNERS HELPED

The results of studies at Pullman, Wash., by the Fruit and Vegetable Products Laboratory in cooperation with the State Agricultural Experiment Station, on the adaptability for canning of Elberta peaches grown in Washington, were reported in four papers published in trade journals. The information given in these papers on the relation of maturity when harvested, and of ripening and storage conditions, to the canning quality of Elberta peaches contributed toward the improvement in quality and increase in quantity of the Washington peach pack in 1944. Preliminary results of processing studies indicated that considerable improvement in the quality of canned Elberta and other freestone peaches packed in the Northwest can be realized by modifying current canning practices. Experiments showed that discoloration does not result from ions of various metals in the sirup.

The freestone peaches from the western part of Washington were less suitable for canning than those from the central part of the State, because they had a greater tendency toward clinging pits. However, they developed less color, especially in the pit cavity, which may prove advantageous.

CANNED CITRUS JUICES IMPROVED IN FLAVOR

Orange-juice concentrates of improved flavor were prepared at the United States Citrus Products Laboratory in Winter Haven, Fla., in cooperation with the Florida Citrus Commission, by evaporating juice under high vacuum to 65° Brix and diluting with a quantity of

fresh whole juice to a final concentration of 40–45° Brix. Substantial amounts of volatile flavoring constituents are thus returned to the product, which can be diluted with water to produce a beverage like fresh orange juice. Storage tests are in progress on samples prepared by several variations of this new procedure, for which patent protection is being sought.

Publication of the previously reported work at the Winter Haven Laboratory on tangerine sirups and beverage-base concentrates resulted in much industrial interest, particularly among carbonated-beverage manufacturers, and samples of these products have been distributed to interested parties.

Preliminary experiments were conducted by the Agricultural Chemical Research Division, in cooperation with the Eastern Regional Research Laboratory, to determine the applicability to citrus juices of the process developed at the Eastern Regional Laboratory for total flavor recovery from apple juice. The pilot-plant equipment used for apples was modified to separate the insoluble-volatile oil fraction continuously while the aqueous flavor essence was being recovered and concentrated. Bacteriological tests showed that the juice was pasteurized in the process of flash distillation of the flavor fractions under conditions that did not produce a cooked flavor in the residual juice. The residual juice was concentrated separately, and various combinations of the flavor essence, volatile oil, and juice concentrate were prepared for storage tests.

The United States Fruit and Vegetable Products Laboratory in Weslaco, Texas, made determinations of the taste appeal and keeping qualities of various blends of Hamlin and Temple orange juice, both alone and in combination with Marsh Seedless grapefruit juice. The most desirable flavor was obtained by combining 60 percent of grapefruit juice with 40 percent of a blend of two parts of Hamlin and one part of Temple orange juice. When sulfur dioxide was used as a preservative, it did not entirely prevent the loss of vitamin C in storage.

GRAPEFRUIT JUICE FROM WESTERN FRUIT MODIFIED FOR CANNING

The Fruit and Vegetable Chemistry Laboratory at Los Angeles has been investigating the possibility of achieving greater uniformity in the quality of canned juice made from California and Arizona grapefruit at different times during the season. Early fruit tends to be sour and bitter. As the season progresses the fruit becomes sweeter and less bitter, the best juice being obtained in midseason. During the latter part of the season the sugar content of the juice remains about the same, but the acidity decreases, making the juice somewhat insipid. Greater uniformity in the sugar-acid ratio of the juice would make it more acceptable to consumers.

Preliminary experiments on grapefruit juice made from selected lots of Arizona grapefruit picked at intervals during the season indicated that juice made early in the season could be improved by adding a buffer salt to raise the pH from about 2.8 to about 3.3 and enough sugar to raise the Brix reading from 10.4° to about 12.5°. The juice from midseason fruit was modified by adding smaller quantities of buffer salt to raise the pH to 3.2 or 3.3; addition of sugar was not necessary. Insipid juice obtained near the end of the season was modified

by addition of citric acid or sodium citrate. The improvement in taste of the modified juices, as compared with that of unmodified control samples, was very striking. Thus far, no method has been devised for ridding the juice of the bitter substance naringen, which is extracted from the pith and rag of any grapefruit by the reaming process.

CITRUS-BYPRODUCT WASTE USED AS RAW MATERIAL IN NEW INDUSTRIES

The production of byproduct feed from citrus-juice canning residues of pulp, peel, and rag leaves unused large volumes of dilute carbohydrate-containing press liquor that constitutes a serious disposal problem. Evaporation of the liquor to a molasses is the basis of a process developed at the United States Citrus Products Laboratory in Winter Haven, Fla., for the fermentation of these carbohydrates to produce alcohol. During the 1944–45 season, alcohol was produced commercially from citrus molasses in a small plant at Lake Alfred, Fla., with technical cooperation and advice from members of the Bureau's personnel.

An alternative use for the dilute press liquor, developed at Winter Haven, is the production of feed yeast from the carbohydrate, mineral, and protein nutrients in the liquor. A commercial firm began full-scale operation of this process during the past season and produced a torula yeast for incorporation with stock feed to increase its protein and vitamin contents.

SUGAR LOSSES FROM BEETS IN STORAGE REDUCED BY WHITEWASHING

In cooperative work on the control of sugar losses during the outdoor storage of sugar beets awaiting processing, it was found that whitewashing the surface of a 150-ton pile of beets reduced the maximum daytime temperatures of the surface beets by as much as 20° F. The consequent lowering of the respiration rate would account for the resulting saving of sugar, which amounted to 8 to 10 pounds per ton of surface beets. Although the benefits of whitewashing are small at depths of more than a foot under the surface, the sugar that can be saved by this procedure should amount to over a million pounds annually, while the cost of the operation is nominal. From the low respiration losses found for beets in the centers of storage piles, it was concluded that the frequently high commercial losses are due largely to microbial spoilage.

SUGARCANE BYPRODUCTS RECOVERED COMMERCIALLY

Practical methods of recovering sugarcane wax in sugar mills by extraction of the clarification muds yield a mixture of dark, hard wax with fatty and unsaponifiable substances. The wax must be separated from the mixture and purified. Heretofore, this has been accomplished by extracting the crude wax (broken into chips) with a fat solvent at room temperature, but such a procedure is not readily adaptable to efficient commercial operation. During the past year a more effective method of purification was developed by the Agricultural Chemical Research Division at the Department's Sugar Plants Field Station in Houma, La. It is based upon the discovery that the hard

wax can be made to crystallize in granular form by melting the crude mixture with a relatively small proportion of wax solvent and allowing the solution to cool slowly. For optimum results the solution should contain about 60 percent of crude wax and be allowed to stand undisturbed for about 18 hours. If there is not too high a proportion of fatty matter and impurities in the crude material, the wax forms separate granular crystals, and addition of a selective fat solvent, such as acetone, permits rapid filtration for removal of fat, which is completed by thoroughly washing the wax crystals with the fat solvent. The solvent remaining on the crystals readily evaporates below the melting point of the wax, which is obtained as a purified, granular product of enhanced commercial value.

The process has been put into operation commercially by one plant, and another firm planned to begin a similar operation in the next cane-grinding season.

The process previously developed for recovering the plastics intermediate, aconitic acid, from sorgo sirup was successfully adapted to the recovery of this product from sugarcane molasses. It was operated on a pilot-plant scale by sugar technologists of the Agricultural Chemical Research Division in cooperation with a commercial firm at its sugar factory in Louisiana. Several tons of crude calcium aconitite were produced from diluted second molasses. A large part of the pilot-plan production was sold by the sugar company to chemical firms interested in the experimental development of uses for aconitic acid and its derivatives. The company planned to install equipment for recovering aconitate from its entire grind of sugarcane next season.

NAVAL STORES INDUSTRY AIDED BY BUREAU'S RESEARCH

During the past fiscal year, the technologists of the Naval Stores Research Division cooperated with commercial firms in the installation and initial operation of several new pine-gum refineries. These firms, like others, have been licensed by the Secretary of Agriculture to use the Bureau's patents on this process. There has been an increase each year in the amount of gum that is cleaned and distilled according to the Bureau's recommendations, with higher yields, better products, and increased income to the gum farmer. A continuous gum-distilling process to replace the present batch process is being evolved and has progressed to the stage of successful pilot-plant runs with prospects of early industrial application.

A method was developed for the liquid-phase isomerization of alpha-pinene to dipentene and allo-ocimene. It was discovered previously that dipentene can be converted to isoprene by a pyrolytic method with yields exceeding 65 percent of theory. Large quantities of isoprene are used by the synthetic rubber industry. Allo-ocimene was previously found to promote rapid drying of oil varnishes and to have properties that should make it useful for synthetic resins.

Soaps made of certain rosin acid derivatives were found to have exceptional value as emulsifying agents in the production of synthetic rubber by copolymerization of butadiene and styrene in an aqueous emulsion.

In efforts to develop substitutes for ester gum (rosin glyceride), a method was developed for making rosin esters of slow-reacting alcohols (such as 2,3-butylene glycol), which ordinarily require 12

to 20 hours for esterification, by first reacting the rosin with lactic acid and then esterifying the reaction product. This method required the relatively short time of 5 to 7 hours. It is applicable to the preparation of rosin esters in general, and was used for the preparation of the glycerol, mannitol, pentaerythritol, butylene glycol, propylene glycol, and octyl alcohol esters of the rosin-lactic acid reaction product.

This Bureau continued to cooperate with the Forest Service in connection with its program for increasing turpentine and rosin production by stimulating the secretion of oleoresin from the cut inner bark of pine trees by treating the streaks with mineral acid. It found that merchantable rosin can be produced if the gum from the acid-treated trees (which often makes opaque rosin) is mixed with gum from untreated trees before stilling. This finding, which was published, contributed toward a wider use of acid stimulation by naval stores producers. The washing step of the Bureau's gum-cleaning process removes any mineral acid.

Statistical data were collected and published quarterly (under the provisions of Public Law 278, 74th Congress) on the production, distribution, industrial consumption, and stocks of naval stores products. In addition, data were collected and tabulated for monthly surveys of naval stores stocks and for monthly reports on production of wood naval stores.

MOLD RESISTANT TREATMENT DEVELOPED FOR LEATHER

In cooperation with the Office of the Chief of Ordnance, a compound and treating procedure were developed at the Eastern Regional Research Laboratory for making leather cases for binoculars and other leather military equipment resistant to mold growth when exposed under conditions of high humidity and temperature. The compound consists of 33 percent paraffin wax, 2.2 percent salicyl anilide, 25 percent isopropyl alcohol, and 39.8 percent mineral spirits. It has been successfully applied to completely fabricated leather equipment, and has given greatly increased resistance to both moisture and mold growth in laboratory tests extending up to eight weeks and in service tests in the Pacific and Panama areas extending up to eight months. In only a few instances has mold developed on the treated articles, and only two mold strains, from among the large number tested, were not inhibited by the treatment. This salicyl anilide-wax treatment for leather was reported by the National Institute of Health to have no irritating effect on human skin and by the Frankford Arsenal to have no deleterious effects on optical instruments. Use of lower wax content, to permit treatment at room temperatures, and of other fungicides were being studied, and the development of protective treatments for civilian use and home application were under consideration.

IMPROVED TALLOW EMULSIFIERS PRODUCED FOR SYNTHETIC RUBBER MANUFACTURE

As noted in the report for 1944, the Eastern Regional Research Laboratory undertook a cooperative investigation of tallow and tallow soaps as a part of the comprehensive research program of the Rubber Reserve Company. Based upon results previously reported, mild

selective hydrogenation of tallows before they are used for the preparation of soap was suggested as the best apparent remedy for the difficulties experienced with tallow soap as an emulsifying agent in the polymerization step of synthetic rubber manufacture. Selective hydrogenation was tried, in pilot plant and regular production, and found to completely eliminate the troublesome variability in tallows.

This collaborative development resulted in an increased rate of polymerization and, for the first time, a fixed production cycle, which, in turn, effected a substantial increase in production capacity of GR–S synthetic rubber plants without any increase in existing plant facilities. Furthermore, the development of a superior grade of emulsifier came at a time when the copolymer plants were changing over to continuous polymerization which requires the utmost uniformity in raw materials and reaction rates.

The spectrophotometric method of analysis, developed at the Eastern Regional Laboratory, was found by the Rubber Reserve Company to be superior to any chemical test or combination of chemical tests for detecting the presence of any residual polyunsaturated fatty acids in the hydrogenated fats and their soaps. Accordingly, this method was adopted for use throughout the industry for control purposes and for incorporation in the new specifications for purchase of the soaps.

The Rubber Reserve Company specified that all of its soap requirements for 1946 (about 130,000,000 pounds) shall be hydrogenated to a uniformly low content of polyunsaturates as shown by spectrophotometric analysis. These requirements can be met by the use of nonedible tallows and greases, edible tallows being no longer required. The research on tallow emulsifiers has not only contributed substantially to the synthetic rubber program, but it has also been instrumental in maintaining a large and important outlet for animal fats.

IMPROVED OLEIC ACID MADE FROM CRUDE ANIMAL FATS OR OILS

By selective hydrogenation of the fatty acids from animal fats or oils having a high ratio of oleic acid to linoleic and other polyunsaturated acids, the proportion of the latter acids can be reduced very readily to 1 percent or less without substantially affecting the oleic acid content. Studies at the Eastern Regional Research Laboratory have shown that such hydrogenated fatty acids can be used for the preparation of refined oleic acid either by the usual method of cold pressing or, preferably, by fractional crystallization from solutions at such temperatures as are necessary to precipitate only the saturated acids. The oleic acid thus produced is substantially free from polyunsaturated acids. If it is desirable to prepare oleic acid having a purity above 95 percent, this can usually be done by subjecting the filtered liquid, after removal of volatile solvent, to fractional distillation under vacuum, for removal of the more volatile palmitic acid.

This process offers an advantage over those previously used for laboratory preparation of purified oleic acid, since it avoids the necessity of separating oleic acid from the polyunsaturated acids and thus eliminates operations at very low temperatures. The product, moreover, is much better than ordinary commercial oleic acid (red oil) with regard to stability of color and odor.

The development of a satisfactory commercial process for the production of refined oleic acid would be an important contribution to the

utilization of fats and oils, particularly the cheap and abundant tallows and greases, for chemical products. The oleic acid of commerce usually contains a total of 25 to 35 percent of saturated and polyunsaturated acids.

NEW NICOTINE COMPOUNDS KILL FUNGI AS WELL AS INSECTS

Although nicotine has long been used as an insecticide, few if any of the compounds derived from the alkaloid have been previously investigated as fungicides. Studies by the Eastern Regional Research Laboratory have shown that two different types of nicotine derivatives have fungicidal as well as insecticidal activity.

Derivatives of one type, double salts of nicotine and metals, were prepared by the combination of nicotine or a nicotine salt with certain organic acid salts of copper, zinc, cobalt, nickel, aluminum, manganese, or iron. For example, cupric dinicotine benzoate was obtained by the reaction of cupric benzoate with nicotine benzoate. Several of the compounds, particularly those containing copper, zinc, or nickel, exhibited both fungicidal and insecticidal properties. In laboratory tests conducted in cooperation with the Pennsylvania Agricultural Experiment Station, the minimum doses of cupric dinicotine benzoate required to kill 50 percent of the spores of *Sclerotinia fructicola*, *Venturia inaequalis*, and *Phytophthora infestans* supplied 0.05, 0.16, and 0.35 microgram of copper per square centimeter of leaf surface, respectively. The corresponding values for Bordeaux mixture were 0.27, 0.16, and 0.30. Tests by the United States Bureau of Plant Industry, Soils, and Agricultural Engineering showed that cupric dinicotine benzoate and cuprous nicotine cyanide retained their toxicity to fungi throughout an 18-day weathering period. Some injury to peach and bean foliage was observed in these latter tests.

Nicotine derivatives of another type, nicotinium salts, were also prepared and tested as fungicides in cooperation with the Rhode Island Agricultural Experiment Station. These nicotinium salts, which contain no metals, were obtained by the reaction of alkyl or aralkyl halides with nicotine. Reaction between the alkyl nicotinium halides and metal salts of fatty acids yielded alkyl nicotinium fatty acid salts and metal halides. Laboratory assays of toxicity to *Macrosporium sarcinaeforme* spores indicated some specific relationships between chemical structure and such toxicity. Derivatives having lauryl and cetyl radicals exhibited much higher toxicity than compounds having benzyl or short-chain alkyl radicals. The more promising members of the series such as lauryl nicotinium bromide, dilauryl nicotinium dichloride, and cetyl nicotinium thiocyanate were being subjected to field tests against apple scab.

THREE NATIVE PLANTS SHOW PROMISE AS SOURCES OF TANNING EXTRACTS

As the supplies of blight-killed chestnut wood become more and more limited, this country will become increasingly dependent on foreign and synthetic tannins unless additional domestic sources are developed. Considerable progress has been made in studies conducted at the Eastern Regional Research Laboratory on three domestic plant materials that show promise as potential tannin sources.

Canaigre.—Field studies were continued in cooperation with the United States Bureau of Plant Industry, Soils, and Agricultural Engineering in Texas, New Mexico, and Arizona. Average tannin contents (moisture-free basis) of roots from selections grown at various locations and harvested in 1944 ranged from 23.1 to 31.3 percent, and roots collected after two years' growth at Sacaton, Ariz., contained 35 percent tannin. The field tests indicated several root strains of superior quality as regards yields, tannin content and purity. The Arizona strains studied were, in general, higher in tannin and purity than those obtained in New Mexico. From experimental plots of canaigre more than eight tons of roots were harvested in 1944. In laboratory tests, the tannin was extracted very successfully from both crushed and powdered samples of canaigre roots from Arizona. Several successive treatments were employed, each involving vigorous mixing of the material with warm water and separation of liquor from solids by centrifugal filtration. Recovery of tannin in the liquors was 77.8 and 80.5 percent, respectively, of the total tannin in the crushed and powdered samples. Acceptable purities in the liquors and concentrated extracts were obtained by removal of sugars by fermentation. The liquors were filtered, concentrated, and dried in a vacuum drum to produce a powdered canaigre extract which, on analysis, showed tannin 62.1 percent, nontannins 29.1 percent, and purity 68.2.

Scrub oak bark.—In cooperation with the Engineering and Industrial Experiment Station of the University of Florida, studies were undertaken on scrub oak bark as a potential source of tannin. Seven areas were inspected, 70 trees sampled, and over 100 samples of bark analyzed for tannin. The average tannin contents of the Turkey oak (*Quercus laevis*) barks from six areas ranged from 9.8 to 11.3 percent on a moisture-free basis. Bluejack oak (*Quercus cinerea*) bark from one area contained 6.5 percent tannin. An improved laboratory procedure for the extraction of tannin was developed by which an extraction efficiency of over 90 percent was attained. From the liquors obtained, a powdered extract was made. On analysis, it showed 61 percent tannin and a purity of 67.

Sumac.—The tanning properties of Sicilian sumac (*Rhus coriaria*) and three domestic sumacs (*R. copallina*, *R. glabra*, and *R. typhina*) were compared in a commercial tanning test on 330 dozen sheepskin skivers. All the sumacs produced leathers of acceptable commercial quality, but the Sicilian sumac produced leather of the lightest color and the best "feel." Dwarf sumac (*R. copallina*) gave leather of the greatest thickness and highest weight yield which was softer and more flexible than the other leathers and ranked second in color. From laboratory experiments it was concluded that, in making sumac extract, the leaves should remain in water for the minimum time consistent with efficient leaching, and the temperature should not exceed 70° C.

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